Issued January 11, 1913.

U. S. DEPARTMENT OF AGRICULTURE,

FOREST SERVICE—Bulletin 119.

HENRY S. GRAVES, Forester.

FOREST PRODUCTS LABORATORY SERIES.

AN EXAMINATION OF THE OLEORESINS OF SOME WESTERN PINES.

BY

A. W. SCHORGER,

Chemist in Forest Products.

WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1913.

FOREST SERVICE.

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LETTER OF TRANSMITTAL.

U. S. DEPARTMENT OF AGRICULTURE,
FOREST SERVICE,
Washington, D. C., July 24, 1912.

SIR: I have the honor to transmit herewith a manuscript entitled "An Examination of the Oleoresins of Some Western Pines," by A. W. Schorger, chemist in forest products, and to recommend its publication as Bulletin 119 of the Forest Service. The samples of oleoresins examined were collected by forest officers in Districts 3 and 5; the chemical work was performed at the Forest Products Laboratory, maintained in cooperation with the University of Wisconsin, at Madison, Wis.

Respectfully,

HENRY S. GRAVES,
Forester.

Hon. JAMES WILSON,
Secretary of Agriculture.

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EXAMINATION OF THE OLEORESINS OF SOME WESTERN PINES.

GENERAL PROPERTIES AND COMPOSITION OF OLEORESINS.

A wound in the sapwood of a growing conifer induces, to a greater or less extent, the flow of a liquid resembling honey in appearance and consistency. This liquid, called oleoresin, consists of a solution of resin acids in a volatile oil.

Turpentine is the trade name applied to the volatile oil; it is also sometimes called "oil of turpentine" or "spirits of turpentine." In Europe the term "oil of turpentine" is invariably used to denote the volatile constituent, while "turpentine" alone signifies the oleoresin. In this country the oleoresin is commercially known as "gum" or "crude turpentine," while "dip" and "scrape" are terms commonly used to signify, respectively, the portions dipped from the receptacles used in turpentine operations or scraped from the scarified faces of the trees.

The turpentine, or volatile oil, is separated from the oleoresin by distillation, and the residue in the still, after being freed from trash, is the colophony or "rosin" of commerce.

Turpentine, from the chemist's standpoint, consists of a mixture of hydrocarbons having the empirical formula $C_{10}H_{16}$, called terpenes. American turpentine consists largely of the terpene α-pinene, with smaller amounts of β-pinene [1] and camphene.[2] French turpentine agrees closely with American turpentine in its physical and chemical properties.

Colophony or rosin is a hard, vitreous, amorphous body, breaking with a conchoidal fracture and varying in color from black to light amber. It consists of monobasic resin acids, which usually can be obtained in a crystalline state by appropriate treatment.

Knowledge of the resin acids, their empirical formula, constitution, and properties is in a very confused state. A large number of resin acids have been described and held to be distinct bodies, but it seems probable that the majority of these are modified forms of one or more typical acids. American colophony is very generally considered to contain from 80 to 95 per cent abietic acid. The physical properties

[1] Schimmel & Co. Report, April, 1908, pp. 99-100.

[2] Ibid., October, 1897, p. 68.

of abietic acid, such as melting point, optical rotation, and crystalline form, depend upon the methods by which the crystalline acid has been isolated;[1] a statement as to the method of isolation is especially necessary when melting points are given. The empirical formula of abietic acid has long been disputed. Numerous investigators have advanced the formula $C_{19}H_{28}O_2$,[2] but the weight of evidence is in favor of the formula $C_{20}H_{30}O_2$.[3]

PURPOSE OF THE STUDY.

Because of the rapid decrease in the supply of longleaf pine and Cuban pine available for the production of naval stores, the Forest Service conducted tapping experiments on several species of western pines to determine their value as a source of turpentine and rosin.[4] The oleoresins of these species were examined to determine to what extent they agree with the similar product obtained from the southern pines. The investigation was purely a chemical one, and no practical experiments were made to ascertain what value the volatile oils would have in the paint and varnish industries. While no one of the oils from the western species agrees entirely with standard gum turpentines, there is no reason to conclude that the oils from several of the species examined will not serve for various industrial purposes.

KINDS OF OLEORESINS EXAMINED.

The oleoresins examined were from western yellow pine (*Pinus ponderosa* Laws.) grown on the Coconino National Forest in Arizona, and from western yellow pine, digger pine (*Pinus sabiniana* Dougl.), lodgepole pine (*Pinus contorta* Loud.), and sugar pine (*Pinus lambertiana* Dougl.) grown on the Sierra National Forest in California. These samples were secured in the fall of 1910. During 1911 the same species were tapped systematically from May to October. The oleoresins representing the collections of the entire period were analyzed also, and the results were entirely in accord with those previously obtained. Therefore, except in a few instances, the results of the later analyses are not given. However, during the year 1911, piñon pine (*Pinus edulis* Engelm.) was tapped on the Montezuma National

[1] Compare Schkateloff, Moniteur Scientifique, pp. 217-227, vol. 22, 1908, and Leskiewicz, Jour. f. prak. Chem., p. 412, vol. 189, 1910.

[2] Compare Tschirch, Die Harze und die Harzbehälter, 2d ed., pp. 670-671, 1906; Mach, Monatsh. für Chemie, p. 186, vol. 14, 1893; ibid., p. 627, vol. 15, 1894; Easterfield and Bagley, Jour. Chem. Soc., p. 1238, vol. 85, 1904; Tschirch and Studer, Archiv. d. Pharm., p. 495, vol. 241, 1903; ibid., p. 5 23; ibid., p. 3, vol. 245, 1907.

[3] Compare Valente, Atti della R. Accad. dei Lincei, p. 13, vol. 1 (4), 1884; Fahrion, Chem. Rev. über Fett- und Harz-Ind., p. 237, 1898; Levy, Zeit. f. angew. Chem., p. 1740, vol. 18, 1905, and Ber. Deutsch. Chem. Ges., p. 3043, vol. 39, 1906; Vesterberg, Ber. Deutsch. Chem. Ges., p. 121, vol. 40, 1907; Koritschoner, Zeit. f. angew. Chem., p. 642, vol. 20, 1907; and Leskiewicz, Jour. f. prak. Chem., p. 412, vol. 189, 1910.

[4] The results of the tapping experiments are given in Forest Service Bulletin 116, "Possibilities of Western Pines as a Source of Naval Stores," by H. S. Betts.

Forest, Colorado, and the analyses made on this species are included. A brief description of the samples upon which the analyses reported in this bulletin were made is here given.

Western yellow pine.—The oleoresin which was obtained from the Sierra National Forest was secured from trees tapped September 13 to October 12, 1910, which grew at an altitude of 4,000 feet. The sample amounted to about 50 pounds. The oleoresin of this species (var. *P. ponderosa scopulorum* Engelm.) sent from the Coconino National Forest in Arizona was obtained from trees tapped August 1 to September 15, 1910. Two dippings were made at intervals of three weeks. About 80 pounds of oleoresin, representing a mixture of both dippings, were shipped. The trees tapped grew at an altitude of 7,300 feet.

Digger pine.—The oleoresin was secured from trees which grew at an altitude of 2,700 feet and were first tapped August 19, 1910. The material shipped amounted to about 50 pounds.

Sugar pine.—The sample was from trees which grew at an altitude of 5,800 feet; they were tapped from September 13 to October 12, 1910. The sample weighed about 5 pounds.

Lodgepole pine.—The trees, at an altitude of 6,000 feet, were tapped from September 13 to October 12, 1910, and the sample weighed about 5 pounds.

Piñon pine.—The oleoresin was secured from trees tapped from June 9 to October 31, 1911. The sample, amounting to 50 pounds, represented the "dip" secured from 5 dippings at 3-weeks intervals.

In all cases the oleoresins were collected by a cup system. The samples were shipped in closed tin cans within from 1 to 4 weeks after collection. A further period, varying from 1 to 2½ months, elapsed before the examination of the samples was begun, during which time the material was retained in the shipping cans. The metal of the cans showed no indications of attack by the crude gum.

METHODS OF EXAMINATION.

OLEORESIN.

The general examination of all the oleoresins was the same. From 350 to 400 grams of the crude resin were distilled with steam in a tared 1.5-liter balloon flask, with a Kjeldahl connecting bulb tube placed between the flask and condenser to prevent any rosin from being carried over mechanically. The rosin remaining in the flask was kept heated until all the water had been expelled, care being taken that the temperature did not exceed 145°. When bubbles ceased to form on the surface of the rosin, on agitation, the removal of the water was considered complete. The rosin was then strained through two layers of fine muslin, and that which adhered was com-

pletely removed by extraction with chloroform in a Soxhlet apparatus. The weight of trash obtained, subtracted from the combined weight of trash and rosin after drying, gave the weight of the rosin. The percentage of water originally in the oleoresin was obtained by difference.[1]

VOLATILE OIL.

The oil for examination was secured by distillation with steam. About 500 grams of this oil were fractionally distilled, using a 12-inch Hempel column, and the specific gravity and refractive index of the fractions were determined with the Westphal balance and Abbe refractometer. The detailed method of fractionation is given in Bulletin 105[2] of the Forest Service.

The methods employed in the chemical examination of the volatile oils will be discussed in connection with the determination of their various constituents.

ROSIN.

The grade of the rosin was determined by comparison with the standard rosin cubes used in the naval stores trade.

The specific gravity was determined by means of a salt solution of such density that a fragment of the rosin, free from cracks and bubbles, remained suspended in it, neither rising nor sinking. The solution was maintained at a temperature of 15° C. and its specific gravity determined with a hydrometer. The specific gravity of the rosin was considered equal to that of the salt solution.

The acid number was obtained by dissolving from 1 to 1.5 grams of rosin in 95 per cent alcohol and titrating the solution directly in the cold, with a N/2 alcoholic potassium hydroxide solution using phenol-pthalein as the indicator. The number of milligrams of potassium hydroxide required to neutralize 1 gram of the rosin represents the acid number.

The saponification number was determined by treating from 1 to 1.5 grams of powdered rosin with 25 cubic centimeters of N/2 alcoholic potassium hydroxide solution. After heating the solution for one-half hour on a steam bath, and then cooling, the excess potassium hydroxide was determined by titration with a N/2 sulphuric acid solution using phenol-pthalein as the indicator. The saponification number represents the number of milligrams of potassium hydroxide neutralized by 1 gram of rosin.

Rosin does not contain esters but contains a small proportion of bodies having the nature of lactones. The measure of the latter

[1] The water may be conveniently determined directly as follows: 100 c. c. of dry redistilled turpentine are added to a given weight of oleoresin (approximately 100 grams) and 100 c. c. of turpentine distilled over by direct heat. The distillate containing all the water is collected in a graduated funnel. On standing a short time the distillate separates into two layers and the amount of water is read off.

[2] "Wood turpentines, their analysis, refining, and composition," by L. F. Hawley.

represents the ether number and is obtained by subtracting the acid number from the saponification number.

The methods of isolating the resin acids will be discussed under the several species, since each species usually requires a different treatment. The composition of the resin acids was checked by means of their silver salts, which were obtained in the following way: A weighed amount of the resin acids was dissolved in alcohol and the solution was exactly neutralized with alcoholic caustic soda. The sodium salt was then decomposed by adding the calculated amount of silver nitrate dissolved in a small amount of water. The precipitate of silver salt was filtered off with a suction pump and the residue washed with water, alcohol, and finally with ether. The precipitate was dried at 60° for half an hour and then allowed to stand a day over sulphuric acid.

ABBREVIATIONS.

The following abbreviations are used:

$d_{15°}$ or "specific gravity" = specific gravity at 15° compared with water at 15°.

$n_{D15°}$ or "index of refraction" = index of refraction at 15°

$a_{D20°}$ = optical rotation at 20° in a 100 mm. tube.

$[a]_D$ = specific rotation.

RESULTS OF EXAMINATIONS BY SPECIES.

Pinus Ponderosa Laws (California).

LITERATURE.

The oleoresin of *Pinus ponderosa*, or western yellow pine, evidently has never been subjected to a careful examination. Sadtler[1] examined an oil coming supposedly from *Pinus ponderosa*. However, since the oil he examined had the general properties of normal heptane, it must have come from either *Pinus sabiniana* or *Pinus jeffreyi*, which, so far as known, are the only species that yield heptane. Confusion between the species might readily occur, because *Pinus jeffreyi* so closely resembles *Pinus ponderosa* that it is often considered a variety. Wenzell[2] had examined in his laboratory a sample of oleoresin from *Pinus ponderosa* obtained from Virginia, Nev., and stated that the odor, specific gravity, and boiling point corresponded with common oil of turpentine. The material examined in the forest products laboratory does not corroborate this statement.

[1] Am. Jour. Pharm., pp. 176–180, vol. 51, 1879.

[2] Pharm. Rev., pp. 165–172, vol. 18, 1900.

EXAMINATION OF THE OLEORESIN.

The oleoresin of the western yellow pine from the Sierra National Forest, Cal., had a specific gravity of 1.0290 at 15°. Following is the average composition shown by four analyses:

	Per cent.
Volatile oil	18.5
Rosin (grade WW, or highest grade)	79.5
Chips, needles, etc	.8
Water (by difference)	1.2
Total	100.0

An analysis of scrape showed the following composition:

	Per cent.
Volatile oil	13.2
Rosin (grade H, or seventh grade)	84.9
Chips, needles, etc	.8
Water by difference	1.1
Total	100.0

EXAMINATION OF THE VOLATILE OIL.

PHYSICAL PROPERTIES.

The specific gravity of the volatile oil was 0.8625; the index of refraction, 1.4772; and the specific rotation, $[a]_D = -14.39°$. On fractionation of 500 grams of oil the results given in Table 1 were obtained:

TABLE 1.—*Fractional distillation of the volatile oil of Pinus ponderosa from the Sierra National Forest, Cal.*

Temperature (corrected).	Distillate.		Specific gravity at 15°.	Index of refraction at 15°.	Specific rotation at 20°.
	Observed.	Cumulative.			
°C.	*Per cent.*	*Per cent.*			
164.0–168.2	5.01	5.01	0.8578	1.4740	−13.81°
168.6	9.94	14.95	.8595	1.4750	−13.70
169.0	9.36	24.31	.8601	1.4752	−13.17
169.2	9.20	33.51	.8606	1.4753	−12.92
170.5	10.45	43.96	.8608	1.4754	−12.73
171.0	10.71	54.67	.8612	1.4757	−12.98
171.6	10.28	64.95	.8615	1.4760	−13.33
172.4	9.69	74.64	.8619	1.4762	−14.17
175.0	10.36	85.20	.8621	1.4763	−17.15
179.5	7.04	92.24	.8631	1.4775	−24.13
179.5+	7.74	99.98	.9186	1.5063	+0.86

IDENTIFICATION OF THE CONSTITUENTS.

α-pinene.—The first fraction was examined for α-pinene. Redistillation over metallic sodium gave two equal fractions boiling between 156° and 164° and 164° and 165° C. The portion boiling between 156° and 164° gave a precipitate with nitrosyl chloride by Wallach's [1] method. The crystalline pinene nitrosochloride sepa-

[1] Annalen, p. 251, vol. 245, 1888.

rated very reluctantly from the mother liquor. The nitrosochloride, after several precipitations from chloroform with methyl alcohol, melted at 103°; the melting point of its nitrolpiperidine was 118°. These results prove the presence of *l*-α-pinene.

β-pinene.—The fractions boiling between 168.2° and 172.4° were redistilled several times and about 60 per cent (based on the original 500 grams) boiled between 165° and 170°. After seven fractionations, the final one made over metallic sodium, 200 grams were obtained having the following properties: Boiling point, 166.6° to 167.6°; specific gravity, 0.8670; index of refraction, 1.4762; specific rotation, $[\alpha]_D = -15.33°$. This fraction was then examined for β-pinene by Wallach's[1] method, which is as follows: The volatile oil was emulsified with 500 c. c. of water and oxidized with 467 grams of potassium permanganate and 100 grams of caustic soda in 5.5 liters of water with careful cooling. The resulting liquor was distilled with steam and 137 grams of oil recovered. After filtration from the manganese sludge and evaporation to two liters, a stream of carbon dioxide being continuously passed through the solution, a copious precipitate of crystalline sodium nopinate was obtained. After being washed with water and then dried the crude sodium nopinate amounted to 13.8 grams. This gives a yield of 21.9 per cent of the sodium salt based on 63 grams of oxidized oil. The yield is comparatively high and shows the purity of the β-pinene fraction. The nopinic acid was liberated with dilute sulphuric acid. After two crystallizations from water it melted at 126°.

Limonene.—The fractions of the original oil boiling above 172.4° and the residues boiling above 170° obtained from the fractionation of the β-pinene fraction were examined for limonene. By repeated distillation two l-rotatory fractions were obtained, as follows: (1) Boiling point, 174° to 175.7°; specific gravity, 0.8621 at 15° C.; (2) boiling point, 175.7° to 178.6°; specific gravity, 0.8608 at 15° C. Fraction 1 when dissolved in glacial acetic acid and treated with a solution of bromine in acetic acid gave a tetrabromide after a small amount of water had been added. The crystalline tetrabromide melted at 104° after several crystallizations from ethylacetate. Fraction 2 was redistilled over sodium, diluted with ether, and treated with dry hydrogen chloride. A dihydrochloride was obtained which melted at 50° C. The results show the presence of *l*-limonene.

EXAMINATION OF THE ROSIN.

A "water white" sample of the rosin had the following properties: Specific gravity, 1.068; acid number, 148.8; saponification number,

[1] Annalen, p. 228, vol. 356, 1907.

161.3; ether number, 12.5. The specific rotation of the rosin was determined for an alcoholic solution, using the formula $[a]_D = \frac{100a}{lpd}$ in which

$a = -0.66°$, the optical rotation in a 1-decimeter tube at 20° C.
$l = 1$, the length of the tube in decimeters.
$p = 6.22$, the number of grams of the substance in 100 grams of the solution.
$d = 0.8239$, the density of the solution.

Therefore, the specific rotation, $[a]_D = -12.88°$.

The coarsely powdered rosin was digested with twice its weight of alcohol containing 25 per cent concentrated hydrochloric acid. The residue yielded about 90 per cent of crude crystals. These crystals, recrystallized from acetone until white, melted at 159° to 160°; the specific rotation, $[a]_D$, is computed from the following values:

$a = -2.61°$ $\quad p = 4.06$ $\quad [a]_D = -78.44°$
$l = 1$ $\quad d = 0.8196$

When allowed to crystallize slowly from dilute acetone and examined under the microscope, the crystals had the exact crystalline form figured by Schkateloff,[1] Mach,[2] and Levy[3] for abietic acid. By rapid crystallization they have the form of triangular plates. This form can be readily obtained by dissolving the abietic acid crystals in acetone and adding water to the solution until it is turbid; as it cools, a mass of crystals immediately forms.

In order to confirm the presence of abietic acid the silver salt of the resin acid was prepared in the manner described on page 11, and its silver content determined. The results of the analysis were:

	Per cent.
0.1396 gram silver salt gave 0.0365 gram silver	=26. 15
.1120 gram silver salt gave .0295 gram silver	=26. 34
Mean	=26. 25

Silver abietate, $Ag(C_{20}H_{29}O_2)$, requires 26.37 per cent of silver.

Schkateloff's[4] method of precipitating the resin acids works very well for the rosin of *Pinus ponderosa*. It consists in saturating an alcoholic solution of the rosin with sulphur dioxide. The resin acids, which crystallize out on cooling, are white and much purer than those obtained by crystallizing from alcohol and hydrochloric acid. No "bleaching" of the color of the alcoholic solution, which Schkateloff noted, was observed, even though the gas was passed in for two hours.

Some of the original rosin was dissolved in acetone and allowed to stand in an ice box overnight. The crystals obtained were purified

[1] Monit. Scientif., p. 218, vol. 22, 1908.
[2] Monatsh. f. Chem., p. 629, vol. 15, 1894.
[3] Berichte, p. 3044, vol. 39, 1906.
[4] Monit. Scientif., p. 223, vol. 22, 1908.

by recrystallization from the same solvent. They softened at 145°, melted at 155°, and were perfectly liquid at 159°.

The fact that the resin acids begin to soften several degrees below their melting point and are not completely liquid until several degrees above it, even when slowly heated, may account, in part, for the diverse melting points recorded. In this work the first appearance of liquefaction has been taken as the melting point.

A portion of the original rosin was subjected to distillation at reduced pressure. The distillate passing over between 245° and 265° C. at 22 mm. solidified to a hard, pale amber mass. After a second crystallization from acetone, snow-white crystals were obtained; these softened at 145°, melted at 150° to 151°, and became completely liquid at 156°. Dissolved in alcohol, they gave the specific rotation, $[a]_D = -54.29°$, computed from the values:

$$a = -0.72° \qquad p = 1.63$$
$$l = 1 \qquad d = 0.8137$$

It is important to note that the crystals obtained in the presence of hydrochloric acid melted at 159° to 160°, those obtained from acetone alone melted at 155°, and those obtained from the rosin distilled under reduced pressure melted at 150° to 151°. Schkateloff [1] claims that the various acids described in the literature are but different modifications of abietic (sylvic) acid, and that, according to the treatment given, the acid varies in melting point and crystalline form. His opinion is in part confirmed by the results given in this bulletin.

CONCLUSIONS.

From the distillation data it has been estimated that the volatile oil of *Pinus ponderosa* from California contains about 5 per cent *l*-α-pinene, 60 to 70 per cent *l*-β-pinene, and 20 to 25 per cent *l*-limonene. The rosin contains about 90 per cent abietic acid.

Pinus Ponderosa scopulorum Engelm. (Arizona).

EXAMINATION OF THE OLEORESIN.

Two analyses of the oleoresin of the Rocky Mountain form of the western yellow pine (*Pinus ponderosa scopulorum*) from the Coconino National Forest, Ariz., gave the following average:

	Per cent.
Volatile oil	19.6
Rosin (grade M, or fourth grade)	75.0
Chips, needles, etc	3.8
Water (by difference[2])	1.6
Total	100.0

[1] Monit. Scientif., pp. 217-227, vol. 22, 1908.

[2] Determined directly, 1.85 per cent.

EXAMINATION OF THE VOLATILE OIL.

PHYSICAL PROPERTIES.

The oil had these properties:[1] Specific gravity, 0.8639 at 15°; index of refraction, 1.4727 at 15°.

The physical constants of the fractions obtained on distillation are shown in Table 2.

TABLE 2.—*Fractional distillation of the volatile oil of Pinus ponderosa scopulorum from the Coconino National Forest, Ariz.*

Temperature (corrected).	Distillate.		$d_{15°}$. Specific gravity at 15°.	$N_{D15°}$ Index of refraction at 15°.
	Observed.	Cumulative.		
°C.	*Per cent.*	*Per cent.*		
157.6–158.5	2.03	2.03	0.8586	1.4686
159.5	9.69	11.72	.8621	1.4701
159.9	9.97	21.69	.8620	1.4702
160.1	10.21	31.90	.8620	1.4705
160.9	10.06	41.96	.8620	1.4706
161.7	9.39	51.35	.8620	1.4711
162.6	9.97	61.32	.8623	1.4714
165.2	9.12	70.44	.8626	1.4722
170.2	10.50	80.94	.8626	1.4735
173.0	5.94	86.88	.8615	1.4752
177.1	6.25	93.13	.8593	1.4758
183.3	2.19	95.32	.8576	1.4769
183.3+	4.60	99.92	.....	.....

The original oil, and especially the last fractions, had a pleasant orange-like odor.

IDENTIFICATION OF THE CONSTITUENTS.

α-pinene.—The first fractions of the oil, when tested for α-pinene, readily yielded a nitrosochloride when treated with nitrosyl chloride; the purified nitrosochloride melted at 103°.

β-pinene.—The fractions boiling between 160° and 170° were examined for β-pinene by oxidation with potassium permanganate in the manner previously described. A small amount of nopinic acid (about 0.75 per cent) was obtained, which melted at 125°; this proved the presence of β-pinene.

Limonene.—The fractions boiling above 170° were repeatedly fractionated and two fractions were separated. These had the following properties: (1) Boiling point, 175° to 176°; specific gravity, 0.8588; (2) boiling point, 176° to 177°; specific gravity, 0.8580. Fraction 1 was distilled over sodium, dissolved in ether and treated with dry hydrogen chloride. A dihydrochloride was obtained, which melted at 50°. Fraction 2 was treated with bromine. The

[1] Two oils obtained from separate areas and representing the collection for the season 1911 had the following properties: (1) specific gravity, 0.8654 at 15°; index of refraction, 1.4723 at 15°; specific rotation, $[\alpha]_D = +13.03°$; (2) specific gravity, 0.8672 at 15°; index of refraction, 1.4729 at 15°; specific rotation, $[\alpha]_D = +12.86°$.

resulting tetrabromide, after several crystallizations from ethyl acetate, melted at 104.5°, the melting point of limonene tetrabromide.

Totally anhydrous reagents, it was found, prevented the precipitation of limonene tetrabromide. The limonene fraction dissolved in glacial acetic acid and treated with bromine gave no trace of a crystalline precipitate after standing in a cool place for two days. When a few drops of water were added, until a faint turbidity was produced, a copious precipitate of limonene tetrabromide soon followed.

Although this species is a variety of *Pinus ponderosa*, there are marked differences in the properties of the two oils, as shown by chemical analysis and inspection of the distillation curves (figs. 1, 2, and 3). All the oils of *Pinus ponderosa* examined were *l*-rotatory, while those of *Pinus ponderosa scopulorum* were *d*-rotatory. The former consisted largely of β-pinene and the latter of α-pinene.

EXAMINATION OF THE ROSIN.

After digestion of the rosin on the steam bath with a mixture of alcohol and concentrated hydrochloric acid, the crystalline residue was recrystallized from 95 per cent alcohol and gave a yield of about 90 per cent of abietic acid. Purified by repeated crystallizations from acetone, the abietic acid melted at 159°.

The original rosin, grade WW, had a specific rotation, $[\alpha]_D = -30.95°$, determined from an 8.29 per cent alcoholic solution. The purified crystals in an alcoholic solution gave the specific rotation $[\alpha]_D = -88.02°$ from the values:

$$a = -1.36° \qquad p = 1.90$$
$$l = 1 \qquad d = 0.8132$$

For further confirmation of the presence of abietic acid, the silver salts were analyzed, with the following results:

	Per cent.
0.3203 gram silver salt gave 0.0834 gram silver	=26.04
.0600 gram silver salt gave .0159 gram silver	=26.50
.1922 gram silver salt gave .0504 gram silver	=26.22
Mean	=26.25

Silver abietate, $Ag(C_{20}H_{29}O_2)$, requires 26.37 per cent silver.

It will be noted that this abietic acid is strongly *l*-rotatory, and it is probable that the lower rotations of other authors is due to a mixture of *d*- and *l*- acids. For the specific rotation of abietic acid Dieterich [1] gives −48°; Haller, [2] −53°; Mach, [3] −69.96°; Mead and Kremers, [4] −53.42°; Leskiewicz [5] (for *l*-sylvic acid), −102.85°. Caillot [6] observed, however, that the optical rotation decreased with

[1] Dissertation, Berne, 1883.
[2] Berichte, p. 2167, vol. 18, 1885.
[3] Monatsh. f. Chemie, p. 641, vol. 14, 1894.
[4] Proc. Am. Pharm. Ass'n, p. 198, vol. 41, 1893.
[5] Jour. f. prak. Chem., p. 416, vol. 189, 1910.
[6] Bull. Soc. Chim., p. 387, vol. 21, 1874.

the degree of heating and with the concentration of the solution. Acids isolated from the oleoresin of *Pinus sabiniana* and not heated above 60° gave −95.82° for the specific rotation, which approaches the rotation of the *l*-sylvic acid for which Leskiewicz found $[\alpha]_D = -102.85°$.

CONCLUSIONS.

From the distillation data it has been estimated that the volatile oil of *Pinus ponderosa scopulorum* contains 60 to 70 per cent *d*-α-pinene, about 5 per cent β-pinene, and 20 to 25 per cent limonene. The rosin contains about 90 per cent abietic acid.

Pinus Sabiniana Dougl.

LITERATURE.[1]

The volatile oil obtained from the resinous exudation of the digger pine (*Pinus sabiniana*), or coming apparently from this species, has been the cause of considerable dispute. That a hydrocarbon, normal heptane, should occur in a growing plant was a source of wonder to phyto-chemists. Semmler (9), in the face of all the investigations that have been carried out on this oil, thinks there is a strong possibility that the material so far examined may have been adulterated with a petroleum hydrocarbon, and recommends the careful examination of the volatile oil obtained from authentic samples of oleoresin.

The question has been further complicated by contradictory statements as to what species of pine really furnished heptane. Wenzell (14), who first discovered "abietene," or heptane, reported it as coming from *Pinus sabiniana* and his later paper (15) is quite conclusive on this point. Sadtler (4) examined an oil having all the properties of "abietene," but coming supposedly from *Pinus ponderosa*.[2] Trimble (11) states that *Pinus jeffreyi* was considered the main source of "abietene," although *Pinus sabiniana* and *Pinus ponderosa* may have furnished samples of "abietene." The papers of Wenzell (15) and Blasdale (1) would indicate that both *Pinus sabiniana* and *Pinus jeffreyi* [3] yield heptane. The thorough chemical investigations by Thorpe (10), Schorlemmer and Thorpe (8), and Venable (12), as well as the work of Venable (13) and Grissom, and Young (16), left little doubt but that the oil from *Pinus sabiniana* is true normal heptane.

[1] The small numbers in parentheses refer to the bibliography on pp. 21-22.

[2] This seems erroneous, since the volatile oil from *Pinus ponderosa* consists of terpenes. (See pp. 12-13 of this paper.)

[3] The oleoresin from *Pinus jeffreyi* has not been examined by the author, but it is hoped that this may be done later.

EXAMINATION OF THE OLEORESIN.

The crude oleoresin which was examined had a characteristic orangelike odor, and white crystals of resin acid had separated out. The specific gravity of the original material was 1.0265; an 8.45 per cent alcoholic solution gave for the optical rotation, $a_{D20°} = -1.26°$. The volatile oil was removed by distillation with steam, and the average of two analyses was as follows:

	Per cent.
Volatile oil	11.4
Rosin (grade M or fourth grade)	83.5
Chips, needles, etc	3.3
Water (by difference)	1.8
Total	100.0

EXAMINATION OF THE VOLATILE OIL.

PHYSICAL PROPERTIES.

The crude oil had a pleasant orangelike odor; specific gravity, 0.6971; and index of refraction, 1.3903. On fractional distillation of 500 grams of the oil the results given in Table 3 were obtained:

TABLE 3.—*Fractional distillation of the volatile oil from Pinus sabiniana.*

Temperature (corrected).	Distillate.		$d_{15°}$ Specific gravity at 15°.	$N_{D15°}$ Index of refraction at 15°.
	Observed.	Cumulative.		
°C.	Per cent.	Per cent.		
96.1–97.3	4.24	4.24	0.6889	1.3890
97.9	7.93	12.17	.6885	1.3898
98.3	9.04	21.21	.6882	1.3898
98.3	8.44	29.65	.6882	1.3898
98.4	8.89	38.54	.6880	1.3898
98.4	8.97	47.51	.6881	1.3898
98.5	8.06	55.57	.6881	1.3898
98.5	7.13	62.70	.6882	1.3898
98.5	6.92	69.62	.6881	1.3898
98.5	6.94	76.56	.6880	1.3899
98.6	6.83	83.39	.6879	1.3899
98.7	6.19	89.58	.6879	1.3899
98.8	5.66	95.24	.6881	1.3900
98.8+	4.66	99.90	.7393	1.4140

IDENTIFICATION OF THE CONSTITUENTS.

Heptane.—It is seen from the data on physical properties given in Table 3 and figure 4 that the crude oil consists of nearly pure heptane, since a single fractionation yields about 90 per cent of an oil with an average boiling point of 98.5°; specific gravity, 0.6881; and index of refraction, 1.3898; the boiling point has been corrected for barometric pressure using the factor 0.045 as determined from the work of Young (16) on the vapor pressures of heptane from *Pinus sabiniana*.

Schimmel & Co.(7) reports that the principal fraction of the oil examined by them boiled between 98.5° and 99° and had a specific gravity of 0.6880 at 15°. Thorpe (10) obtained the following results on a carefully purified oil: boiling point, 98.42° at 760 mm.; specific gravity, 0.70057 at 0°; refractive index for $D = 1.3879$.

During the distillation of the oleoresin with steam, the last portion of oil coming over had a yellow color and a sharp, penetrating odor. On fractionation of the volatile oil, the fractions had only a faint orange odor, while the residue was colored yellow and had a decidedly higher specific gravity (0.7393), and index of refraction (1.4140), and a strong orange odor. The characteristic odor of the crude oil is apparently due to this yellow oil, which on fractionation becomes concentrated in the residue. Thorpe (10) attributes the odor to a "resenoid matter," while Rabak (3) considers it an ester.

Previous investigators have, in general, found a decidedly higher boiling point for the crude oil. Wenzell (14) gives the boiling point at 101° to 115°, the fractions boiling steadily at 101°. Rabak (3) found it to boil at 100° to 101° and Sadtler (4) at 101° to 103°.

EXAMINATION OF THE ROSIN.

The rosin, grade M, had a specific gravity of 1.073; acid number, 156.7; saponification number, 176.5; and ether number, 19.8; a 5.58 per cent alcoholic solution gave the optical rotation, $a_{D20°} = +0.38°$. Rabak (3) states that both the oleoresin and colophony are optically inactive. This statement has not been found to be true of either substance.

All attempts to obtain a crystalline body from the original rosin failed. It seems to be in an amorphous state, noncrystallizable under normal conditions. It was then subjected to distillation in vacuo. Laurent [1] as long ago as 1839 found that the resin acids could be distilled under reduced pressure and the distillate recrystallized. This method has been frequently employed since that time. Rosin is but slightly decomposed under such treatment, and the resin acids recovered are isomers of the formula $C_{20}H_{30}O_2$.

The rosin distilled between 240° and 255° C. at 10 mm. pressure. The viscous distillate solidified on cooling to a hard, transparent, slightly yellow mass, resembling colophony. A portion of the distillate was dissolved in acetone and the solution allowed to stand in a cool place for several days. Large crystals were thus obtained absolutely without color. These were stirred rapidly with small amounts of cold acetone to remove adhering mother liquor, and the solvent was decanted. The crystals were then dissolved in acetone and yielded a colorless solution. Recrystallized twice from the same solvent,

[1] Ann. de Chim et de Phys., p. 383, vol. 72 (2), 1839.

FIG. 1.—RESIN CRYSTALS FROM PINUS SABINIANA; FORMED BY RAPIDLY CRYSTALLIZING, FROM ALCOHOL AND HYDROCHLORIC ACID, THE RESIN ACIDS OBTAINED FROM THE ORIGINAL OLEORESIN.

FIG. 2.—RESIN CRYSTALS FROM PINUS SABINIANA; FORMED BY CRYSTALLIZING, FROM ACETONE, THE PRODUCT OBTAINED BY DISTILLING THE ROSIN UNDER REDUCED PRESSURE.

the crystals softened at 144°, melted at 151° to 152°, and were completely liquid at 158°. Analysis of the silver salt of the crystals gave:

	Per cent.
0.4689 gram silver salt gave 0.1226 gram of Ag or	26.15
Calculated for Ag ($C_{20}H_{29}O_2$)	26.37

The crystals from the crude oleoresin were next examined. A portion of the white crystalline mass which had settled to the bottom of the container was pressed in a hand press, and nearly all the liquid constituents were thus removed. Another method was found to give equally satisfactory results: The crude resinous mass was thrown into a wide Büchner funnel, using silk bolting cloth as a filter; the resin was spread out in a thin layer and suction applied. After two hours a white crystalline mass remained, no longer sticky to the touch, and practically free from volatile oil. After several crystallizations from acetone, finally from methyl alcohol, the crystals melted at 131°; a higher melting point was not obtained. The alcoholic solution of the crystals was strongly *l*-rotatory. The specific rotation, $[a]_D = -95.82°$, was determined from the following values:

$a = -3.74°$ $\quad p = 4.764$

$l = 1$ $\quad d = .8193$

Some of the crystals were dissolved in alcohol and a few drops of concentrated hydrochloric acid added. On cooling, crystals were obtained, in the form of triangular plates, which melted at 158° to 159°. (See Pl. I.) The silver salt of these crystals gave, on analysis, the following results:

	Per cent.
0.2840 gram silver salt gave 0.0751 gram silver	=26.44
Calculated for Ag ($C_{20}H_{29}O_2$)	=26.37

CONCLUSIONS.

The volatile oil from *Pinus sabiniana* consists almost entirely of normal heptane. The rosin probably consists of a noncrystallizable form of abietic acid. The rosin distilled under reduced pressure and the crude oleoresin furnished crystalline resin acids of the formula $C_{20}H_{30}O_2$, and it may be assumed that the rosin consists of amorphous acids of the same composition.

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Pinus Lambertiana Dougl.

EXAMINATION OF THE OLEORESIN.

The crude oleoresin from sugar pine (*Pinus lambertiana*) had a specific gravity of 1.0420. The average composition of two analyses follows:

	Per cent.
Volatile oil	16.4
Rosin (grade H or seventh grade)	75.3
Chips, needles, etc	3.4
Water (by difference)	4.9
Total	100.0

The oleoresin was stringy, contaminated with needles and fine dust, and foamed badly on distillation with steam; the last portion of volatile oil was removed with great difficulty.

A portion of one sample was heated until it became fluid (about 90° C.) and then filtered. An analysis gave the following results:

	Per cent.
Volatile oil	16.2
Rosin (grade K or fifth grade)	82.0
Dirt	0.1
Water (by difference)	1.7
Total	100.0

The filtered material gave a rosin two grades higher than that obtained from the original oleoresin, which well illustrates the effect of trash in darkening the color. From the examination of various

oleoresins it has been found that those of a stringy, viscous, and homogeneous character foam badly on distillation, give up their volatile oil with difficulty, and yield a much darker rosin than is to be expected from "virgin gum." On the other hand, oleoresins, from which the resin acids crystallize and settle out on standing, distill quietly and yield light rosins. The foaming and darkening of the rosin is due partly to the presence of trash, such as needles and chips, and partly to the absorption of oxygen previous to distillation.

EXAMINATION OF THE VOLATILE OIL.

PHYSICAL PROPERTIES.

An oil obtained from oleoresin collected during 1911 had the following properties: Specific gravity, 0.8663; index of refraction, 1.4728; specific rotation, $[a]_D = +10.42°$. Another sample of the oil, amounting approximately to 375 grams, the analysis of which is given in Table 4, had a specific gravity of 0.8658 and an index of refraction of 1.4727.

TABLE 4.—*Fractional distillation of the volatile oil of Pinus lambertiana.*

Temperature (corrected).	Distillate.		$d_{15°}$ Specific gravity at 15° C.	$N_{D15°}$ Index of refraction at 15° C.
	Observed.	Cumulative.		
Degrees, centigrade.	*Per cent.*	*Per cent.*		
155.8–157.3	2.98	2.98	0.8531	1.4657
158.6	9.33	12.31	.8620	1.4693
158.9	10.78	23.09	.8629	1.4698
159.3	10.34	33.43	.8632	1.4701
159.7	10.70	44.13	.8633	1.4703
160.3	9.79	53.92	.8633	1.4708
161.3	9.94	63.86	.8634	1.4716
162.5	9.54	73.40	.8633	1.4726
168.4	7.67	81.07	.8624	1.4736
178.8	5.11	86.18	.8548	1.4721
178.8+	13.62	99.80	.9011	1.4912

IDENTIFICATION OF THE CONSTITUENTS.

α-pinene.—The physical properties of the fractions show that the oil consists largely of α-pinene. For further proof a *d*-rotatory fraction ($a_{D20°} = +13.08°$) boiling between 156° and 157° was treated with nitrosyl chloride. The pinene nitrosochloride obtained from this treatment melted at 103° after several precipitations from chloroform with methyl alcohol.

β-pinene.—That portion of the oil boiling between 160° and 168° was oxidized with potassium permanganate to determine the presence of β-pinene. A small amount of nopinic acid, the characteristic oxidation product of β-pinene, was obtained. The acid melted at 125°.

Phellandrene.—By repeated fractionation about 10 c. c. of oil boiling between 169° and 174.5° with a specific gravity of 0.8550 was obtained. When 5 c. c. were treated with bromine, no crystalline derivative was obtained, indicating the absence of limonene; with N_2O_3 a copious crystalline precipitate was obtained, which, when filtered with a force pump, suddenly decomposed into an amorphous mass that could not again be obtained in a crystalline state. It is probable that a small amount of phellandrene was present.

Aliphatic hydrocarbon.—The residue boiling above 178.8°, which amounted to 13.5 per cent, was distilled at 25 mm. pressure—one-fourth distilled between 110° and 130° and the remainder between 130° and 145°. The portion boiling between 110° and 130° at 25 mm. was split up into four fractions whose specific gravities and indices of refraction showed that it could not consist of terpenes. These fractions were accordingly combined and treated with concentrated sulphuric acid until no further reaction was caused by the addition of more acid. The residual oil boiled between 194° and 201° C. at 742.7 mm.; the specific gravity was 0.7549 and the index of refraction, 1.4249. The decrease in the index of refraction of the tenth fraction, shown in Table 4, must be due to this oil, since all terpenes of as high a boiling point have a much higher index of refraction. From its physical and chemical properties this oil may be a hydrocarbon of the paraffin series. Owing to the small amount of material available for analysis no more definite information could be obtained. The results are based on analysis of material collected during the years 1910 and 1911.

Aromadendrene.—The portion of the residue boiling between 130° and 145° at 25 mm. pressure consisted of a sesquiterpene. It did not yield a crystalline derivative with Br, N_2O_3, or HCl. The carefully purified oil had the following properties: Boiling point, 144° to 148° at 30 mm. (250° to 255° at 739.9 mm.); specific gravity, 0.9238; index of refraction, 1.5006; specific rotation, $[a]_D = +37.88°$ determined from a 33.33 per cent ethereal solution. When a few drops were dissolved in glacial acetic acid in a test tube, and bromine vapors were allowed to flow into the tube, a series of beautiful color reactions were obtained. The solution first turned crimson, then violet, and on standing 5 to 10 minutes became a deep blue. In its physical properties and color reactions the sesquiterpene from *Pinus lambertiana* agrees well with the sesquiterpene "aromadendrene," described by Smith[1] as occurring in Australian eucalyptus oils. Aromadendrene shows the color reactions given above, boils between 260° and 265° C. at atmospheric pressure, and has a specific gravity of 0.9229 to 0.9249 at 19° C.

[1] Jour. and Proc. Roy. Soc. N. S. W., pp. 124-126, vol. 25, 1901.

EXAMINATION OF THE ROSIN.

A sample of H rosin had a specific gravity of 1.078; acid number, 142.7; saponification number, 152.6; ether number, 9.9. The rosin distilled at 250° to 275° at 30 mm. pressure. The viscous distillate hardened to a light yellow, amorphous mass on cooling. Attempts to secure a crystalline resin acid from the original rosin and its distillation product were unsuccessful.

CONCLUSIONS.

From the distillation data it has been estimated that the volatile oil of the sugar pine consists of 70 to 75 per cent *d*-α-pinene; about 5 per cent β-pinene; 2 to 3 per cent of a terpene, probably phellandrene; 2 to 3 per cent of what appears to be an aliphatic hydrocarbon; and 10 to 12 per cent of a sesquiterpene which agrees well in its properties with those of "aromadendrene." The portions of the oil boiling between 170° to 210° C. should be investigated further.

Pinus Contorta Loud.

LITERATURE.

Blasdale [1] examined the oil obtained from oleoresin scraped from peeled lodgepole pines (*Pinus murrayana*).[2] He states that the major portion of the oil distilled between 158° and 160°, but portions boiled as high as 180°. The fraction boiling between 158° and 160° had a specific gravity of 0.8640; an index of refraction of 1.4765; and specific rotation, $[\alpha]_D = -15° 23'$. Without further examination the oil is stated to "consist of terpenes."

EXAMINATION OF THE OLEORESIN.

The crude material which was examined by the author had a specific gravity of 1.0210 and gave on analysis the following percentages:

	Per cent.
Volatile oil	14.7
Rosin (grade I or sixth grade)	77.7
Chips, needles, etc.	2.5
Water (by difference)	5.1
Total	100.0

The oleoresin was very dark, stringy, and badly contaminated with needles, chips, and fine dirt. It foamed excessively on distillation with steam, and the last traces of oil were removed only with difficulty.

[1] Jour. Am. Chem. Soc., pp. 163–164, vol. 23, 1901.

[2] A distinction is no longer maintained between *Pinus contorta* and *Pinus murrayana*.

EXAMINATION OF THE VOLATILE OIL.

PHYSICAL PROPERTIES.

The original oil from the oleoresin collected during the summer of 1911 had the following properties: Specific gravity, 0.8518; index of refraction, 1.4862; specific rotation, $[a]_D = -20.12°$. The oil examined from oleoresin collected in 1910 had: Specific gravity, 0.8549; index of refraction, 1.4860. About 400 grams of the latter oil were submitted to fractional distillation with the results shown in Table 5.

TABLE 5.—*Fractional distillation of the volatile oil from Pinus contorta.*

Temperature (corrected).	Distillate.		$d_{15°}$ Specific gravity at 15°.	$N_{D5°}$ Index of refraction at 15°.
	Observed.	Cumulative.		
° Centigrade.	*Per cent.*	*Per cent.*		
164.4–170.6	2.89	2.89	0.8547	1.4793
171.6	8.55	11.44	.8546	1.4814
172.6	9.08	20.52	.8542	1.4823
173.6	10.77	31.29	.8534	1.4835
175.3	10.22	41.51	.8522	1.4852
177.2	9.79	51.30	.8514	1.4861
177.6	10.03	61.33	.8507	1.4871
177.9	10.23	71.56	.8502	1.4880
178.4	9.26	80.82	.8498	1.4891
178.9	4.15	84.97	.8498	1.4894
178.9+	14.83	99.80	.....	.....

The oil had a very characteristic odor; it was pungent when freshly distilled and, after standing some time, was orange-like. The oil polymerized very considerably at its boiling point. The 15 per cent residue remaining in the distilling flask solidified to a solid, amber-colored mass resembling colophony, insoluble in alcohol, but soluble in ether and chloroform. To avoid loss of oil by polymerization it must be distilled under reduced pressure. The oil carefully purified and finally distilled over metallic sodium, had the following properties: Boiling point, 60° at 11 mm.; specific gravity, $\frac{21°}{15°}$ 0.8460; refractive index, 1.4861; specific rotation, $[a]_D = -12.36°$.

IDENTIFICATION OF CONSTITUENTS.

α-pinene.—The first fraction was redistilled over metallic sodium and tested for α-pinene by treatment with ethyl nitrite and hydrochloric acid. No crystalline nitrosochloride or blue coloration was obtained; however, the failure to secure a precipitate is not conclusive proof of the absence of α-pinene,[1] especially when the oil is highly active.[2]

Phellandrene.—The ease with which the oil polymerized, and its physical properties, pointed to phellandrene. When the original oil was treated with potassium nitrite and acetic acid, or when any

[1] Wallach: Annalen, p. 6, vol. 368, 1909.

[2] Tilden: Jour. Chem. Soc., p. 759, vol. 85, 1904; also Kremers: Pharm. Rundschau, p. 135, vol. 13, 1895.

of its fractions were so treated, a copious precipitate of phellandrene nitrite was obtained. After repeatedly dissolving in chloroform and precipitating with methyl alcohol the nitrite melted at 90° when slowly heated, and at 103° when heated rapidly.

From the data obtained on fractionation it was thought that perhaps both α- and β-phellandrene were present. Wallach [1] states: "β-phellandrene appears to possess a somewhat lower boiling point and higher specific gravity than α-phellandrene." He shows, also, the existence of an α- and β-nitrite of α-phellandrene, and an α- and β-nitrite of β-phellandrene melting at 112° to 113° or 113° to 114°, 105°, 102°, and 97° to 98°,[2] respectively. These melting points were obtained by Wallach, through rapid heating. Although the data in Table 5 and the curves of figures 1 and 2 indicate strongly that both forms of phellandrene are present, in no case was it possible to obtain a nitrite of lower, or higher, melting point from any of the fractions by solution of the nitrite in acetone, and fractional precipitation with water, if the nitrite was purified until perfectly white. Examination for limonene also gave negative results. The oil must, therefore, consist largely of β-phellandrene. So far as known, this terpene has never before been detected in the oil from the oleoresin of any member of the genus *Pinus*.

EXAMINATION OF THE ROSIN.

The rosin was not completely soluble in 95 per cent alcohol. A white curdy residue was obtained, which indicated the presence of some of the oil that had been polymerized during distillation. In appearance it is exactly like the polymerized residue from the distilled oil when digested with alcohol. The oil accordingly polymerizes with great readiness, for the distillation was conducted with steam, and the temperature of 145° C. was not exceeded in drying the rosin.

The rosin, grade I, had the following properties: Specific gravity, 1.061; acid number, 131.2; saponification number, 139.6; ether number, 8.4. About 80 per cent of crude crystals in the form of triangular plates, and melting at 155°, were obtained by crystallization from alcohol, diluted with concentrated HCl. After several crystallizations from acetone the abietic acid melted at 159° to 160°.

For further confirmation, the silver salt of the abietic acid was obtained and analyzed with the following results:

	Per cent.
0.2340 gram silver salt gave 0.0611 gram silver	=26.11
.2470 gram silver salt gave .0647 gram silver	=26.19
Mean	=26.15

Silver abietate, $Ag(C_{20}H_{29}O_2)$, requires 26.37 per cent silver.

[1] Annalen, pp. 42–43, vol. 336, 1904.

[2] Ibid., pp. 15 and 44.

CONCLUSIONS.

The volatile oil of *Pinus contorta* consists almost entirely of *l*-β-phellandrene. The colophony contains about 80 per cent abietic acid.

Pinus edulis Engelm.

EXAMINATION OF THE OLEORESIN.

The oleoresin of piñon pine (*Pinus edulis*) contains very large resin acid crystals and has a characteristic odor resembling *thuja* leaf oil. It has a specific gravity of 1.0238.

The average composition as shown by the analysis of five consecutive dippings is:

	Per cent.
Volatile oil	20.0
Rosin (grade I to WG)	76.5
Trash	0.9
Water (by difference)	2.6
Total	100.0

EXAMINATION OF THE VOLATILE OIL.

PHYSICAL PROPERTIES.

The oil had the characteristic odor of the oleoresin, due to the presence of a sesquiterpene; the specific gravity was 0.8680; the index of refraction, 1.4707; and the specific rotation $[a]_D = +19.26°$. On fractional distillation the results shown in table 6 were obtained:

TABLE 6.—*Fractional distillation of the volatile oil of Pinus edulis*

Temperature (corrected).	Distillate.		$d15°$ Specific gravity at 15° C.	$N_{D15°}$ Index of refraction at 15° C.
	Observed.	Cumulative.		
Degrees Centigrade.	*Per cent.*	*Per cent.*		
155.9–157.4	5.10	5.10	0.8617	1.4677
157.6	10.66	15.76	.8617	1.4683
157.9	10.28	26.04	.8621	1.4687
158.4	8.99	35.03	.8619	1.4689
158.9	10.54	45.57	.8616	1.4689
160.0	11.04	56.61	.8611	1.4693
162.4	8.76	65.37	.8609	1.4696
176.5	9.72	75.09	.8605	1.4713
194.9	3.87	78.96	.8616	1.4723
194.9+	20.74	99.70	.9129	1.4837

IDENTIFICATION OF CONSTITUENTS.

α-pinene.—The results obtained on fractional distillation show that the oil consists largely of α-pinene. For further confirmation the d-rotatory first fraction was treated with nitrosyl chloride; the pinene nitrosochloride obtained melted at 103° after purification.

Table 6 shows that the specific gravity of the fractions gradually decreases from the third to the ninth fraction. This may be due to the presence of a small amount of limonene. However, on redistillation, about 90 per cent of the fractions which first boiled between 162.4° and 194.9°, boiled between 156° and 165°, which showed that they consist largely of pinene. The higher boiling point on the first distillation may be explained by the retarding effect of the large amount of high boiling sesquiterpene present.

β-pinene.—The portion which boiled between 160° and 170° on redistillation, amounting to 12 per cent, was oxidized with $K_2Mn_2O_8$. About 0.5 per cent of nopinic acid, the characteristic oxidation product of β-pinene, was recovered; it melted at 123°.

Cadinene.—The residue boiling above 194.9° distilled between 118° and 145° at 20 mm. pressure. A fraction representing 50 per cent of the total was collected between 135° and 140°, the specific gravity of which was 0.9173, the index of refraction 1.4925 and the specific rotation $[a]_D = +15.41°$; the color was faint green. This fraction, to which the characteristic odor of the original oil is due, gave a dihydrochloride melting at 118°. A 5.94 per cent solution of the dihydrochloride in ether gave the optical rotation $a_{D20°} = -1.89°$. Cadinene is accordingly the sesquiterpene present. When five drops of the cadinene fraction were dissolved in 2 c. c. of acetic anhydride and a drop of concentrated sulphuric acid added a green color was produced, which became blue, then purple, and finally red. When glacial acetic acid [1] is used in place of acetic anhydride a red color is produced almost immediately. This appears to be the first recorded occurrence of cadinene in a turpentine oil.

EXAMINATION OF THE ROSIN.

A sample of WG rosin had the following properties: Specific gravity, 1.060; acid number, 155.2; saponification number, 164.1; ether number, 8.9. The rosin distilled between 240° to 255° at 10 mm. pressure. A few long prismatic crystals formed on the sides of the receiver, but could not be isolated because of adherent oily products. The viscous distillate hardened to a faint yellow, amorphous mass. All attempts to secure a crystalline body from either the original rosin or the distilled rosin were unsuccessful.

A portion of the white resin acids from the original oleoresin, which had settled to the bottom of the container, was pressed in a hand press until the greater portion of the intermingled liquid products had been removed. The white, waxy cake, after four crystallizations from acetone, yielded crystals melting at 129° to 130°. When these were dissolved in hot absolute alcohol, and a few drops

[1] Compare Wallach, Annalen, p. 87, vol. 238, 1887.

of concentrated hydrochloric acid were added, microscopic triangular plates separated on cooling. These plates melted at 137° and were completely liquid at 148°. The activity of the resin acid was determined in an alcoholic solution, the specific rotation, $[a]_D = -52.77°$, being computed from the following values:

$$a = -0.57° \qquad p = 1.33$$
$$l = 1 \qquad d = 0.8122$$

Analysis of the silver salt of the resin acid gave the following results:

	Per cent.
0.1867 gram silver salt gave 0.0494 gram silver	=26.46
Calculated for $Ag(C_{20}H_{29}O_2)$	=26.37

CONCLUSIONS.

From the distillation data it has been estimated that the volatile oil from the oleoresin of *Pinus edulis* contains approximately 70 to 75 per cent α-pinene, about 5 per cent β-pinene, and 15 to 20 per cent *d*-cadinene. The oleoresin yields a resin acid of the formula $C_{20}H_{30}O_2$; although no crystalline resin acid was obtained from the colophony it may be assumed to consist of amorphous acids of the preceding formula.

SUMMARY.

With the exception of the digger pine, the volatile oil from all the species examined consists of terpenes ($C_{10}H_{16}$), and sesquiterpenes ($C_{15}H_{24}$). The oil from the digger pine consists of the hydrocarbon heptane (C_7H_{16}), a normal constituent of petroleum.

COMPARISONS WITH COMMERCIAL NAVAL STORES.

VOLATILE OIL.

In Table 7 and in figures 1 to 4 the various oils examined are compared with an average gum turpentine which consists of a mixture of the volatile oils of the Cuban pine (*Pinus heterophylla* Ell.) and longleaf pine (*Pinus palustris* Mill.):

TABLE 7.—*Characteristics of the volatile oil from the oleoresin of various pines.*

Source of oil.	$N_{D15°}$ Index of refraction at 15° C.	$d_{15°}$. Specific gravity at 15° C.	Boiling points of first 90 per cent of the distillate.	Principal constituent.
Western yellow pine, California	1.4772	0.8625	164.0 to 177.5°C	β-pinene.
Western yellow pine, Arizona	1.4727	.8639	157.6 to 175.0	α-pinene.
Digger pine, California	1.3903	.6971	96.2 to 98.8	Heptane.
Sugar pine, California	1.4727	.8658	155.8 to 180.0	α-pinene
Lodgepole pine, California	1.4860	.8549	164.4 to 179.0	β-phellandrene.
Piñon pine, Colorado	1.4707	.8680	[1]	α-pinene.
Gum turpentine [2]	1.4730	.8685	156 to 165	α-pinene.

[1] The first 80 per cent distills between 156° and 200° C. [2] From Cuban and longleaf pines.

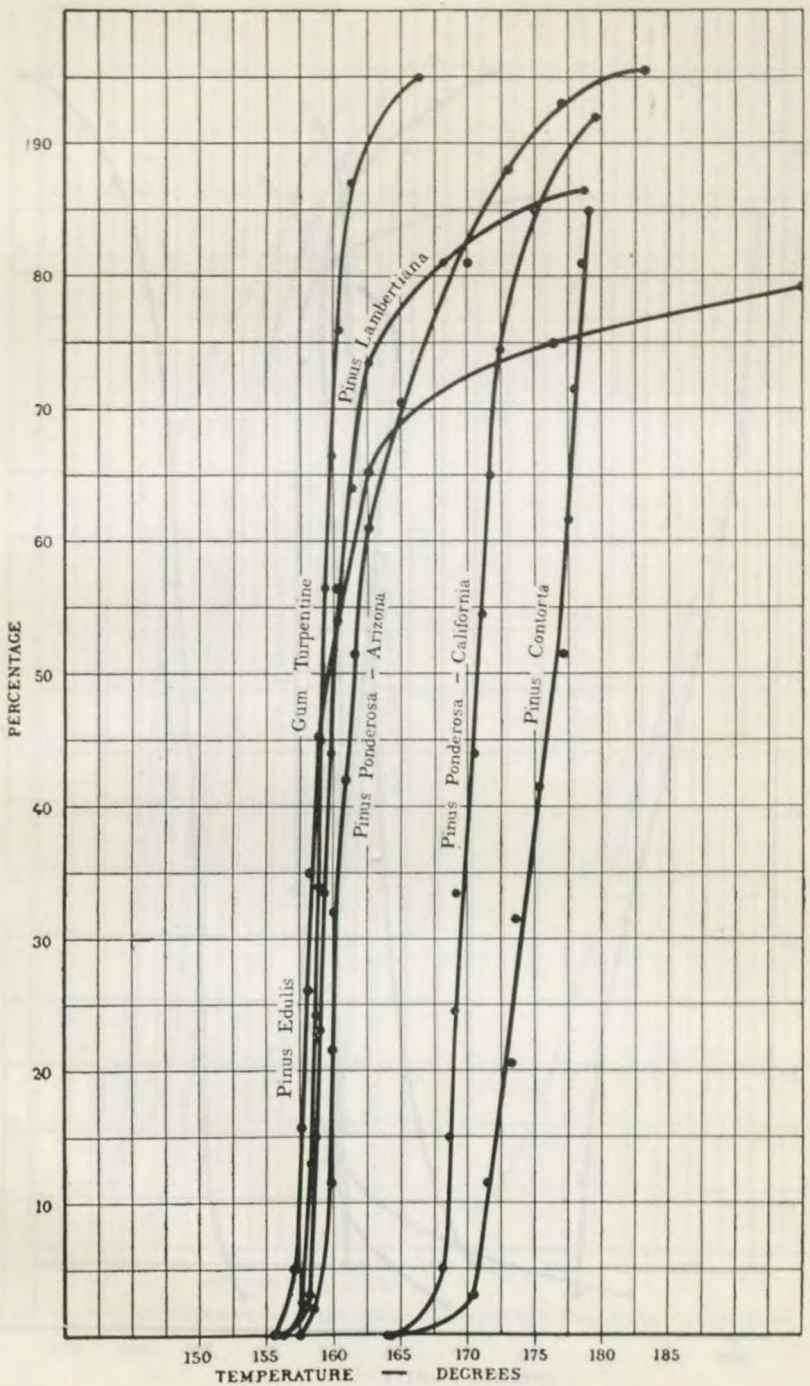

FIG. 1.—Boiling-point curves for the volatile oil obtained from the oleoresin of various pines.

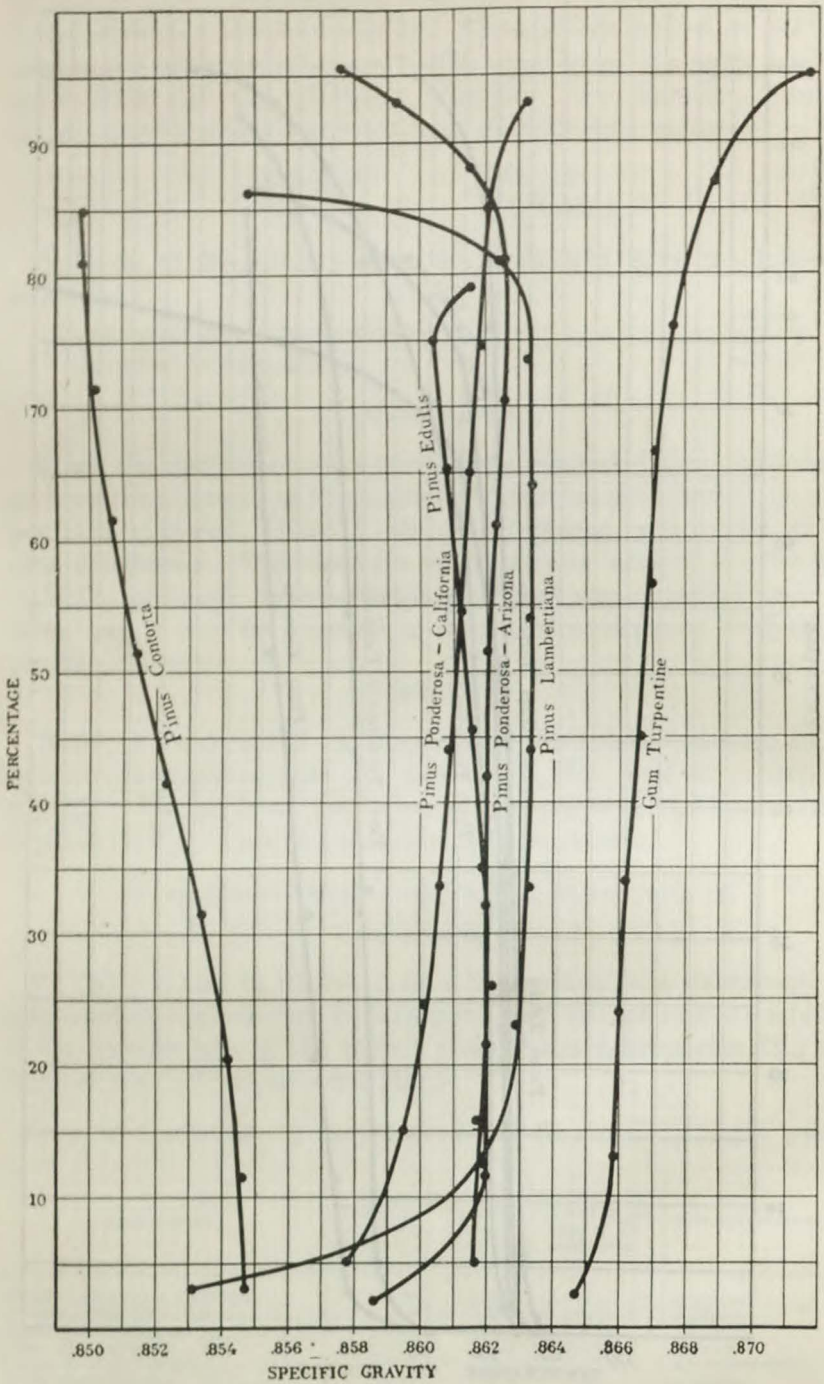

FIG. 2.—Specific-gravity curves for the volatile oil obtained from the oleoresin of various pines.

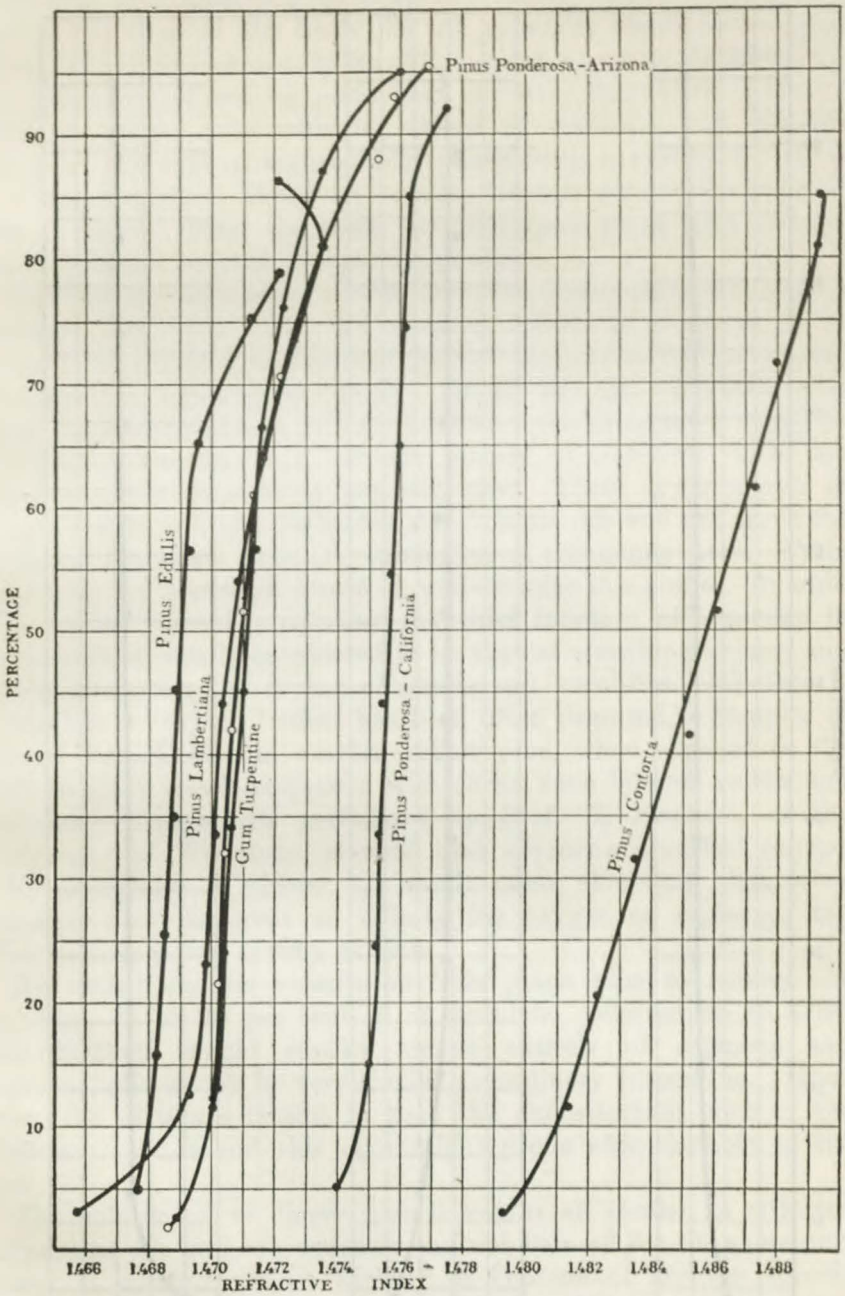

FIG. 3.—Index of refraction curves for the volatile oil obtained from the oleoresin of various pines.

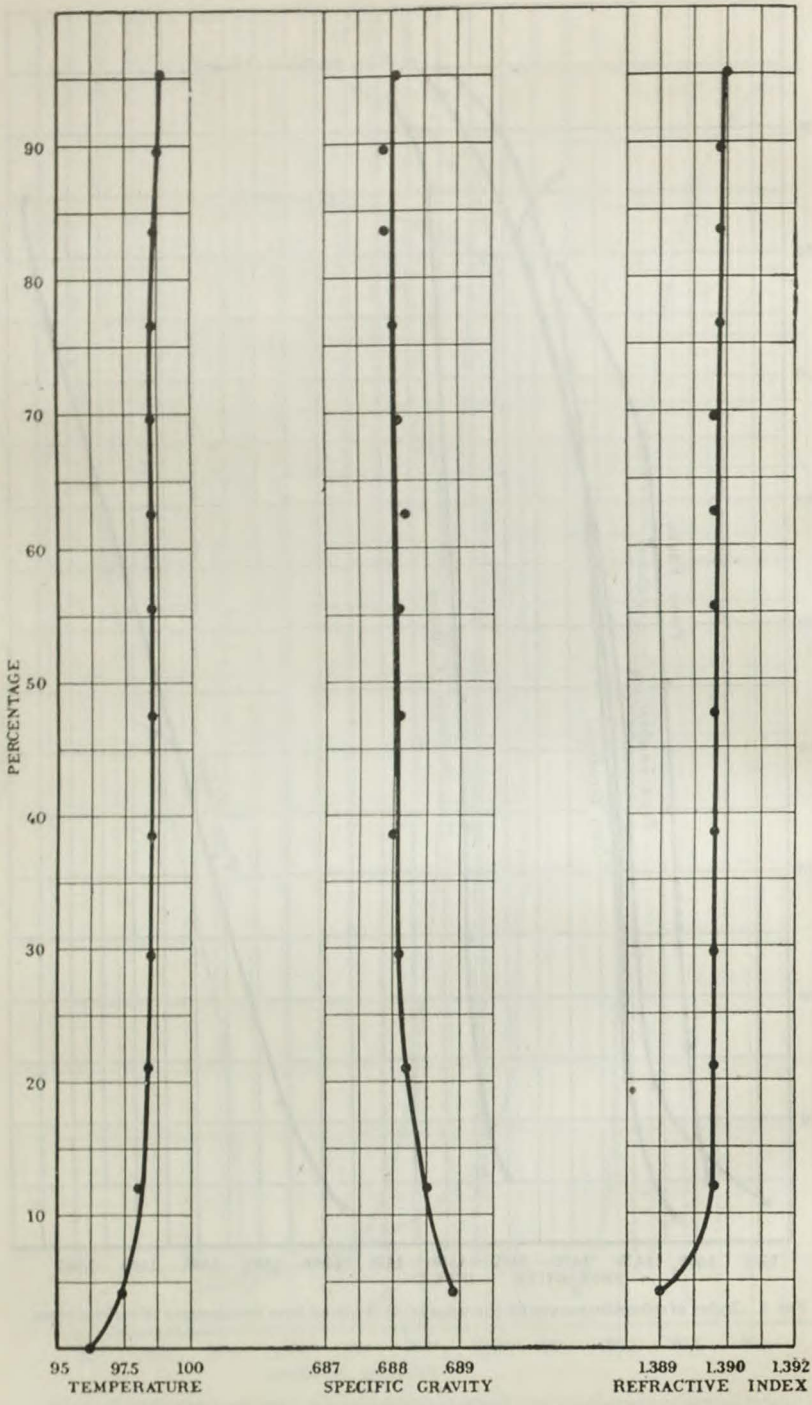

FIG. 4.—Boiling point, specific gravity, and index of refraction curves for the volatile oil from the oleoresin of *Pinus sabiniana*.

French and American turpentines consist largely of α-pinene and 95 per cent of the fresh oils will generally distill below 170°. The oil of lodgepole pine consists of the unstable terpene phellandrene, and has a higher boiling point than ordinary turpentine. The oil from the sugar pine consists mainly of α-pinene, but contains about 25 per cent of high-boiling constituents, a portion of which is a sesquiterpene. However, because there is an extremely small flow of "gum" from the sugar and lodgepole pines their volatile oils will hardly become commercial products.

The oil from the western yellow pine from California distills largely between 168° and 172° and consists mainly of β-pinene. The latter is a normal constituent of "gum" turpentine and invariably accompanies α-pinene in nature. Of all the oils examined, that from the western yellow pine from Arizona conforms most nearly to ordinary turpentine. It consists largely of α-pinene with but small amounts of β-pinene and limonene. There is no reason to suppose that both the California and Arizona oils will not serve the purposes for which ordinary turpentine is commonly used. Practical tests are necessary, however, to determine this point. In addition to its solvent properties the chief function of α-pinene in turpentine is usually considered to be that of absorbing oxygen and hence promoting the drying of paints and varnishes. Whether it really has a "drying" effect has been often disputed.[1] Samples of the oil from California western yellow pine, when exposed to the light in glass vessels stoppered with corks, soon became yellow and resinous. Experiments performed by Prof. E. Kremers, of the University of Wisconsin, showed that limonene absorbed oxygen fully as rapidly as pinene. It would seem, therefore, that other terpenes have as great an affinity for oxygen as α-pinene, and their solvent power is fully as great.

By redistilling the volatile oil from piñon pine to remove the cadinene 75 to 80 per cent of oil could be collected up to 175°; this distillate would consist almost entirely of α-pinene and β-pinene, and would be very similar to ordinary turpentine. However, the distillate retains in part the characteristic odor of the cadinene residue and this odor might prove objectionable to the user.

The volatile oil of digger pine is not at all similar to ordinary turpentine oils and consequently can not be used for the same purpose. It consists almost entirely of heptane of uniform specific gravity and boiling point. It is readily purified by agitation with a small amount of concentrated sulphuric acid. Various industries should find in this a cheap and valuable solvent where uniformity is required.

[1] Compare Powney, "The influence of solvents on the drying of linseed oil," Analyst, pp. 192–198, vol. 35, 1910.

ROSIN.

Table 8 contains the constants of the various "rosins" as well as the constants of a sample of commercial rosin from the Southern States which represents a mixture of colophony from the longleaf and Cuban pines:

TABLE 8.—*Chemical and physical constants of rosins from various species.*

Source of "rosin."	Grade.	$d_{15°}$. Specific gravity at 15° C.	Acid number.	Saponification number.	Ether number.
Western yellow pine, California	WW	1.068	148.8	161.3	12.5
Digger pine	M	1.073	156.7	176.5	19.8
Sugar pine	H	1.078	142.7	152.6	9.9
Lodgepole pine	I	1.061	131.2	139.6	8.4
Piñon pine	WG	1.060	155.2	164.1	8.9
Cuban and longleaf pine mixed	WW	.....	161.5	170.4	8.9

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